

LAID-OPEN PATENT GAZETTE OF THE JAPANESE PATENT OFFICE (JP) (A)

Laid-Open Number: 58/113,208

Laid-Open Date: July 6, 1983

Filing Number: 56/209,847

Filing Date: December 28, 1981

Int. Cl.³: C 08 F 10/00, 2/34

Inventors: Akifumi Kato, Shigeo Uenaga
and Ryoichi Yamamoto

Applicant: Mitsui Petrochemical Co., Ltd.

Representatives: Heikichi Odajima, Patent Attorney
and one more

CONTINUOUS VAPOR-PHASE POLYMERIZATION OF OLEFINS

What is Claimed is:

1. In a vapor-phase polymerization of olefins by which a continuous vapor-phase polymerization is carried out while forming a fluidized bed phase in a vessel equipped with a stirrer, a method of continuous vapor-phase polymerization of olefins which is characterized in that

(i) a vapor-phase polymerization is carried out while stirring the fluidized bed phase zone in such a manner that an

upper end of a stirring blade of the said stirrer is buried in the said zone; and

(ii) the pressure difference is monitored between (a) the zone within a fluidized bed phase zone which is located just above the upper end of the said stirring blade and (b) just above the top of the said fluidized bed phase zone, and olefin polymer is taken out from the said zone in such a manner that the height of the said fluidized bed phase zone is kept almost constant according to the pressure difference.

2. A method according to claim 1 in which the height of the said fluidized bed phase zone is within a range of 1.02- to 1.4-fold of the height of the upper end of the said stirring blade.

3. A method according to claim 1 or claim 2 in which a gas flow rate in the said fluidized bed phase zone is made 1-60 cm/second.

Detailed Description of the Invention:

The present invention relates to a method for a vapor-phase polymerization of olefins. More particularly, it relates to a method for a continuous vapor-phase polymerization of olefins in which stable operation can be continuously carried out for long time whereby the manufacture of an olefin polymer

of a consistent quality is possible.

The present invention specifically relates to, in a vapor-phase polymerization of olefins by which a continuous vapor-phase polymerization is carried out while forming a fluidized bed phase in a vessel equipped with a stirrer, a method of continuous vapor-phase polymerization of olefins which is characterized in that

(i) a vapor-phase polymerization is carried out while stirring the fluidized bed phase zone in such a manner that an upper end of a stirring blade of the said stirrer is buried in the said zone; and

(ii) the pressure difference is monitored between (a) the zone within a fluidized bed phase zone which is located just above the upper end of the said stirring blade and (b) just above the top of the said fluidized bed phase zone, and olefin polymer is taken out from the said zone in such a manner that the height of the said fluidized bed phase zone is kept almost constant according to the pressure difference.

It has been known that, in a vapor-phase polymerization vessel equipped with a stirrer, a gaseous olefin is blown into an olefin polymer particle layer containing a catalyst to form a fluidized bed whereby the olefin is continuously subjected to a vapor-phase polymerization.

In such a case, an attempt has been known where the gas flow rate is made smaller and, nevertheless, a good mixing state is achieved by stirring the fluidized bed phase by a mechanical stirring so that entrainment of fine olefin polymer particles or catalyst particles is prevented. However, in spite of such an attempt, it is difficult to make the mixing state in the fluidized bed phase zone uniform and, therefore, it is often noted that masses of the olefin polymer are produced and they block out the inlet for the gas and the outlet for the olefin polymer whereby an operation for long time becomes impossible. In addition, when such a vapor-phase polymerization is carried out continuously, it is necessary to discharge the olefin polymer so that the height of the fluidized bed phase zone is kept as constant as possible in order that a homogeneous polymer may be obtained and a stable operation is carried out.

For such a purpose, there is an idea that the height of the fluidized bed phase zone is measured, and opening and closing of the exhaust valve for the polymer are adjusted for keeping the said height constant. Based upon such an idea, the present inventors have attempted a method for measuring the height of the fluidized bed phase zone in which two pressure detecting elements are set at upper and lower zones in the vapor-phase polymerization vessel where one of them is set in

an upper space zone which is above the fluidized bed phase zone while the other is set at the upper end of the fluidized bed phase zone or within the fluidized bed phase zone and for determining the height of the fluidized bed phase zone by measuring the pressure difference between the two.

The result was that, when the second pressure detecting element is set at the upper end of the fluidized bed phase zone, it is unavoidable to adopt the following control system. Thus, when the upper end of the fluidized bed phase zone reaches the pressure detecting element, the pressure difference from the above-mentioned upper space zone is will be developed, through the detection of which an exhaust valve for the polymer is opened according to the pressure difference detected; the height of the fluidized bed phase zone lowers corresponding to the said exhaustion and is in a lower level than the second detector element; and when that is detected whereby the said exhaust valve for polymer is closed. However, according to such a means, it is not possible to conduct a control whereby a fine tuning of the height of the fluidized bed phase zone is made possible in terms of its operation, and it has been found that there are disadvantages that variations in the height of the fluidized bed phase zone are considerably large and that a stable operation is not easy.

On the other hand, when the second pressure detecting element is set within a fluidized bed phase zone, it has been found that the detecting element is affected by a stirrer depending upon where the element is set and accordingly that the pressure is not correctly detected and an adjustment of the height of the fluidized bed phase zone to a constant level is difficult. It has been further found that there is inconvenience that the said detecting element is apt to be blocked and, in some cases, measurement is not possible. When a measurement is carried out in the area where the stirring the fluidized bed phase is not well stirred, such inconvenience does not occur. However, it has been found that, if such a stirring condition is adopted, formation of uniform fluidized bed for stable polymerization is inhibited and there results a trouble of formation of polymer in blocks.

As a result of a further invention, however, it has been found that, when a method for detecting the above pressure difference is adopted under the above-mentioned conditions (i) and (ii), the height of the fluidized bed phase zone can be controlled to an almost constant height and, in addition, a good mixed state of the fluidized bed phase is achieved whereby a stable polymerization is possible, and troubles such as formation of polymer blocks and adhesion of the polymer to walls

can be prevented. Accordingly, an objective of the present invention is to offer an improved method for a continuous vapor-phase polymerization of olefins.

In the polymerization of olefins according to the present invention, a catalyst is continuously supplied to a fluidized bed phase zone consisting of olefin polymer and catalyst under a stirring condition in a stationary state and, at the same time, gaseous olefin is blown in from the lower part of the said fluidized bed phase zone whereupon the fluidized state is maintained and the polymerization takes place. In the fluidized bed phase zone, stirring is carried out by a stirrer or, preferably, by a stirrer of anchor type whereby a good mixing state can be resulted even to the lateral direction.

The lower end part (bottom) of the fluidized bed phase zone is preferably in a form of a perforated plate for assisting a uniform dispersion of the gaseous olefin and also for preventing the falling of polymer particles, etc. Hydrogen can be used to adjust molecular weight and it may be supplied from the lower end of the fluidized bed phase zone together with the gaseous olefin or may be directly supplied to the fluidized bed phase zone.

With regard to the fluidized bed phase zone of the polymerization vessel, the shape of a head-cut cone or a column

is preferably used. The stirrer or, preferably, that of anchor type which is used in the present invention is in such a structure that the stirring blades rotate near the bottom (usually consisting of a perforated plate) and side wall of the fluidized layer in a shape of a heat-cut cone or a column as mentioned above and the structure is usually made in such a manner that there are stirring blades which extend from the rotating axis to near the side wall along the bottom of the fluidized bed phase zone and further extend upward along the side wall. The heights of the stirring blades are not necessarily the same. The stirrer of anchor type may be equipped with auxiliary stirring blades or may be in a modified design so far as it has the above-mentioned fundamental structure.

During the polymerization of an olefin, it is recommended to take out the olefin polymer continuously or intermittently so that the height of the fluidized bed phase zone is maintained at preferably 1.02- to 1.4-fold or, more preferably, from 1.02- to 1.2-fold of the height to the upper end of the blades of the stirrer and further that variation in the height of the fluidized bed phase zone is preferably kept to a minimum. The height to the upper end of the stirring blades of the stirrer is a distance from the bottom of the fluidized bed phase zone to the upper end of the said stirring blades and, when there

are two or more stirring blades and their heights are different, the highest one is taken as a reference.

In the present invention, the stirring blades are operated so that they are embedded in the fluidized bed phase zone. If a part of the upper area of the stirring blades is outside the fluidized bed phase zone and extends to the upper space zone, adhesion or caking of the olefin polymer takes place at that area, inhibiting stable operation. When the height of the fluidized bed phase zone is kept higher than the above-mentioned preferred range, mixing of the total fluidized bed phase zone system becomes generally insufficient, and adhesion to wall etc. may occur. Therefore, it is recommended to appropriately keep within the above-mentioned preferred range. When a stirrer of anchor type is used and the height of the fluidized bed phase zone is preferably adjusted to an appropriate position within the above-mentioned range, it is now possible to prevent adhesion to the wall and caking of the polymer and to conduct a stable operation as well.

Further, as a result of taking such a constitution, the height of the fluidized bed phase zone can be correctly measured by a pressure difference method and, accordingly, an automatic control is possible by instructing the opening and the closing of the exhaust valve for the olefin polymer according to the

detected pressure difference so as to keep the height of the said zone almost constant. Thus, when the pressure difference between the fluidized bed phase zone and the upper space zone is measured, it is possible to measure the height of the fluidized bed. Usually, however, the pressure detector in the fluidized bed phase zone is apt to be blocked up and, in addition, it is apt to be affected by the stirrer. But, when the height of the fluidized bed phase zone is preferably kept at around 1.02- to 1.4-fold of the height to the upper end of the stirring blades and a detecting element within a fluidized bed phase zone is set at the position which is above the upper end of the stirring blades in the fluidized zone, neither blocking up nor influence from the stirrer takes place and, accordingly, a correct measurement can be carried out for a long period. As a result thereof, it is now possible by means of a pressure detecting element placed within the fluidized bed phase zone and a pressure detecting element in the upper space zone to detect the pressure difference between the two zones and to take out the olefin polymer so as to keep the height of the fluidized bed phase zone almost constant according to the pressure difference detected, whereby a continuous operation for a long period can be automatically carried out. Position of the pressure detecting element at the side of the fluidized bed is

to be made preferably 1.05- to 1.15-fold of the height to the upper end of the stirring blades.

In the present invention, it is also possible to adopt, together with the above-mentioned control, an embodiment where still another pressure detecting element placed within set at a little above the pressure detecting element in the fluidized bed phase zone, the pressure difference between that and the pressure detecting element above the fluidized bed is measured and the upper limit of the height of the fluidized bed phase zone is controlled by the said pressure difference.

Polymerization of olefin in accordance with the present invention covers not only a homopolymerization of an olefin but also copolymerization of olefins or that of an olefin with a diene. Examples of the olefins are ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and 1-decene. The present invention is particularly suitable for the manufacture of a crystalline polymer mainly consisting of ethylene or propylene where, for example, 90% or more of such a monomer are contained.

With regard to a catalyst for the polymerization, various catalytic systems such as a Ziegler catalyst and a Phillips catalyst may be used. For example, a compound of titanium, vanadium, chromium, zirconium, etc. may be used as a catalytic

component. The use of an organoaluminum compound as a catalytic component and a titanium catalyst component supported on a magnesium compound is particularly advantageous because of a high catalytic activity. Such catalytic systems have been widely known already. With an objective of controlling the molecular weight, the molecular weight distribution, the stereoregularity, etc., various additives such as hydrogen, electron donor, halogen compound etc. may be used. Such catalytic components and additives may be supplied to any place of the polymerization vessel. In addition, with an objective of removing heat during the polymerization, it is also possible that easily-volatile inert hydrocarbon is made co-existed. Such a substance plays a role of removal of heat when vaporized in the polymerization vessel.

Although the temperature of polymerization of olefin may vary depending upon the type of the olefin, a temperature range of from about 30°C to about 90°C is usually adopted. Pressure for the polymerization may be anything provided that it is lower than the pressure where the olefin is liquefied and, for example, it is from about 2 to about 30 kg/cm².G.

It is preferred to blow in the olefins from the lower part of the fluidized bed phase zone at a linear velocity of from 1 to 60 cm/second or, particularly, from about 3 to about 40

cm/second. Liquid olefins may be supplied to the polymerization vessel for removal of the heat of polymerization. When a liquid olefin is supplied, it is preferred to supply it to the place above the fluidized bed.

The olefin polymer is taken out either continuously or intermittently from the side of the fluidized bed phase zone so as to maintain the height of the fluidized bed to be constant. It is possible to conduct the continuous polymerization for a long period by adopting such a method.

An embodiment of the present invention is given in Fig. 1. After olefin is polymerized in advance in a preliminary polymerization vessel (1) using an organoaluminum compound component and a titanium catalyst component supported on a magnesium compound, it is continuously supplied to a fluidized bed phase zone (3) of the vapor-phase polymerization vessel via a pipe (11). Additional organoaluminum compound is supplied to a fluidized bed phase zone (3) of the polymerization vessel from a pipe (12). The fluidized bed phase zone (3) which is a reaction bed in the vapor-phase polymerization vessel is stirred by a stirrer (4) in a shape of an anchor. Gaseous olefin which is not condensed in a condenser (6) is supplied to the lower part of the polymerization vessel from a pipe (13) or newly from another pipe (14), and comes to a fluidized bed phase zone

(3) via a perforated plate (5) to fluidize the reaction floor and also to be used for the polymerization. Hydrogen used for the adjustment of the molecular weight is supplied to the polymerization vessel from a pipe (15). Unreacted olefin discharged from the polymerization vessel passes through a pipe (6), is condensed in a condenser (6), passes through a pipe (17) and is sprinkled on a reaction floor from a sprinkler (18).

With regard to the height of the fluidized bed phase zone (3), the pressure difference between the lower pressure line (20) having a detecting element in the upper space zone (2) and the higher pressure line (21) having a detecting element at a position above the upper end (h_1) of the stirring blade in the fluidized bed phase zone (3) is measured by a level meter (23) and the polymer (19) is taken out from a pipe (19) by instructing the opening and the closing of the level control valve (24) so as to keep the height (h_2) of the fluidized bed phase zone constant. In order to prevent the blocking up of the higher pressure line (21), it is recommended to flow a purge gas from a pipe (22).

Example 1.

<Preparation of Titanium Catalyst Component>

Commercially available anhydrous magnesium chloride (30 g), 7.5 ml of ethyl benzoate and 4.5 ml of methyl polysiloxane

(viscosity: 20 c.s. at 25°C) were made to contact for 40 hours using a vibrating ball mill in a nitrogen atmosphere. The resulting processed solid (20 g) was suspended in 200 ml of TiCl_4 and made to contact at 80°C for two hours while stirring. After completion of the reaction, the supernatant liquid was washed with pure hexane by means of a decantation. This operation was repeatedly carried out until no chlorine was detected in the supernatant hexane. The resulting titanium catalyst component contained 65% by weight of chlorine and 1.9% by weight of titanium in terms of atoms. After the above operation was repeated for several times, the product was subjected to the subsequent polymerization.

<Preliminary Polymerization Treatment>

The treatment was conducted in hexane using 1.5 mmol/liter of the above-prepared titanium catalyst component, 6 mmol/liter of triethyl aluminum (hereinafter, referred to as TEA), 2 mmol/liter of methyl p-toluate and propylene which was in an amount of two-fold of the titanium catalyst component.

<Vapor-Phase Polymerization of Polypropylene>

Polymerization was carried out in accordance with a flow diagram as shown in Fig. 1 using the preliminarily polymerized catalyst as mentioned above.

The inner diameter of the vapor-phase polymerization

vessel was 300 mm, the height (h_1) from the perforated plate (5) to the upper end of the height of the stirring blades of the anchor-shaped stirrer (4) was 450 mm, the higher pressure line (21) was made of SUS having an inner diameter of 2 mm, and the pressure detecting element for the fluidized bed phase zone was inserted to the position which was 150 mm from the inner wall of the polymerization vessel and was 30 mm above the upper end of the stirring blades.

While the anchor-shaped stirrer was rotated at 200 rpm, 1 mmol/hour (in terms of titanium atoms) of the titanium catalyst component which had been subjected to the above preliminary polymerization treatment, 50 mmol/hour of TEA, 12 mmol/hour of MPT and propylene gas (including a circulating gas) at a rate of 4 cm (in the polymerization vessel)/second or liquid propylene at a rate of 45 kg/hour were/was sprinkled from a sprinkler (18) and a continuous polymerization of propylene was carried out under the condition of 70 °C polymerization temperature and 18 kg/cm².G polymerization pressure. Further, the polymer was taken out from the pipe (19) at a rate of 10 kg/hour according to the instruction of a level meter so as to make the height (h_2) of the fluidized bed phase zone from the porous plate 490 mm. Incidentally, for prevention of the blocking-out of the higher pressure line, propylene gas was

supplied from a pipe (22) at a rate of 100 Nl/hour.

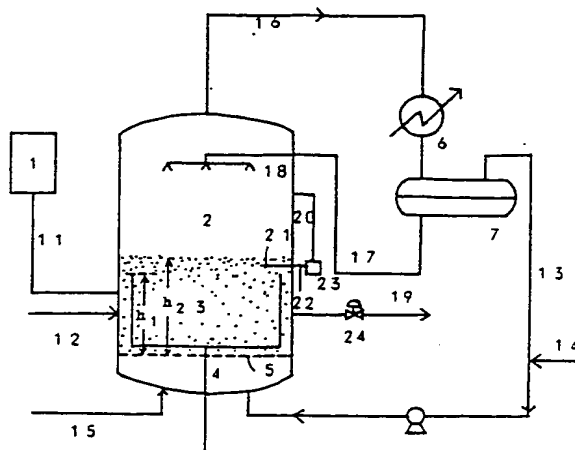
Polypropylene where $MI = 9.1$ and n-heptane-insoluble matters = 93.3% by weight was able to be manufactured in a stable manner for a long period.

Comparative Example.

When the position of the detecting element of the higher pressure line (21) was made at the height of the stirring blades and made 440 mm below the upper end of the stirrer, detection of the level was difficult in any of the cases whereby it was not possible to detect the increase or the decrease of the level.

Brief Explanation of the Drawing:

Attached Fig. 1 is a schematic drawing of the apparatus showing an embodiment of the present invention.

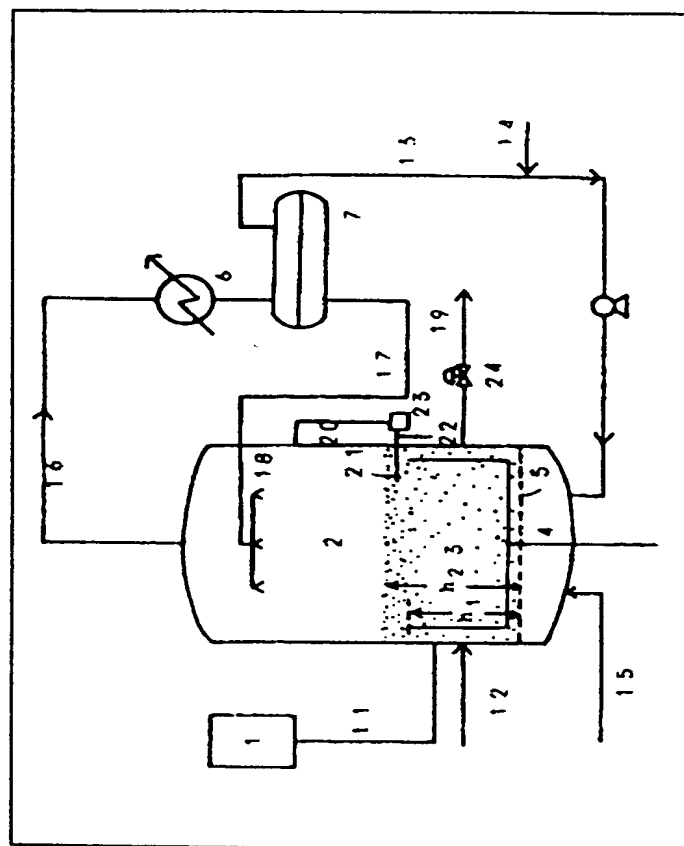


===== WPI =====

- TI - Continuous vapour phase polymerisation of olefin(s) - with pressure difference between stirring blade in fluidised bed and upper phase controlling removal of polymer
- AB - J58113208 The process comprises carrying out vapour polymerization while stirring the fluidised bed phase zone with upper part of a stirring buried in the fluidised bed. The pressure difference is measured between two zones by pressure detecting elements which are set at positions above the upper end of the stirring blade in the fluidised bed phase zone and in the upper space zone. The removal of olefin polymer from the fluidised bed phase zone in accordance with the pressure difference so as to keep height of the fluidised bed phase zone almost constant. In the vapour phase polymerization process for olefins the fluidised bed phase is continuously formed under stirring in a vapour phase polymerization vessel with stirring machine.
- As height of fluidized bed phase zone can be controlled almost constantly then good mixing conditions are obtd. in the fluidised bed phase zone. Polymerization is carried out stably and prodn. of block polymer or adhesion of polymer to the wall of the polymerization vessel can be prevented. (0/1)
- PN - JP58113208 A 830706 DW8333 005pp
 - JP3032562B B 910513 DW9123 000pp
- PR - JP810209847 811228
- PA - (MITC) MITSUI PETROCHEM IND CO LTD
- MC - A04-G01A A10-B
- DC - A17
- IC - C08F2/34 ;C08F10/00
- AN - 83-737298 [33]

===== PAJ =====

- TI - CONTINUOUS VAPOR PHASE POLYMERIZATION OF OLEFIN
- AB - PURPOSE: To obtain an uniform olefin polymer in stable condition, by carrying out an agitation, in a vapor phase polymerizer, so that the upper end of the agitating blade is imbedded in the fluidized bed zone, and detecting a pressure difference between said zone and the upper space to maintain the height of the above zone constant.
- CONSTITUTION: An olefin is preliminarily polymerized in a prepolymerizer 1 followed by continuously feeding the resultant intermediate product to a vapor phase polymerizer equipped with an agitator 4. While agitating the fluidized bed zone 3 so that the upper end of the agitating blade is imbedded in said zone 3, a pressure difference between said zone 3 and the space 2 above the zone 3 is detected through the pressure-detecting element 20 in the space 2 and the other element 21 set at a site within said zone 3 and higher than said upper end of the agitating blade. The olefin polymer produced is drawn through the pipe 19 according to the pressure difference value so that the height of said zone 3 is maintained to a nearly constant level, thus obtaining the objective polymer.
- PN - JP58113208 - 830706
- PD - 83-07-06
- ABD - 830920
- ABV - 007213
- AP - JP810209847 811228
- GR - C187
- PA - MITSUI SEKIYU KAGAKU KOGYO KK
- IN - KATOU AKIFUMI; others: 02
- I - C08F10/00; C08F2/34



⑫ 公開特許公報 (A)

昭58—113208

⑪ Int. Cl.³
C 08 F 10/00
2/34

識別記号

庁内整理番号
7823—4 J
7102—4 J

⑬ 公開 昭和58年(1983) 7 月 6 日

発明の数 1
審査請求 未請求

(全 5 頁)

⑭ オレフィン類の連続気相重合方法

⑮ 特 願 昭56—209847

⑯ 出 願 昭56(1981)12月28日

⑰ 発 明 者 加藤章文
大竹市新町二丁目12番 3 号

⑱ 発 明 者 上永成男
大竹市御園一丁目 3 番27号

⑲ 発 明 者 山本良一

山口県玖珂郡和木町和木四丁目
9 番11号

⑳ 出 願 人 三井石油化学工業株式会社
東京都千代田区霞が関 3 丁目 2
番 5 号

㉑ 代 理 人 弁理士 小田島平吉 外 1 名

明 細 書

1. 発明の名称

オレフィン類の連続気相重合方法

2. 特許請求の範囲

(i) 攪拌器を具備した気相重合槽中で、攪拌条件下に流動床層を形成させながら連続的に気相重合を行うオレフィン類の気相重合方法に於て、

(ii) 該攪拌器の攪拌翼の高さ上端部が該流動床層区域中に埋没する状態で該区域を攪拌しながら気相重合を行うこと、

(iii) 該流動床層区域中で且つ該攪拌翼高さ上端部を超える位置に設けた流動床層区域内圧力検出端と、該流動床層区域より上方の上部空間区域に設けた上部空間区域内圧力検出端とにより、該両区域間の差圧を検知し、この検知された差圧に応じて、該流動床層区域高さがほぼ一定に維持されるように、該区域からオレフィン重合体を抜き出すこと、
を特徴とするオレフィン類の連続気相重合方

法。

(2) 該流動床層区域高さが、該攪拌翼の高さ上端部までの高さの 1.02～1.4 倍の範囲にある特許請求の範囲第 1 項に記載の方法。

(3) 該流動床層内のガス流速を 1～60 cm/秒とする特許請求の範囲第 1 項もしくは第 2 項記載の方法。

3. 発明の詳細な説明

本発明はオレフィン類の気相重合方法に関する。さらに詳しくは長期間連続して安定な運転が可能であり、したがって一定品質のオレフィン重合体の製造が可能なオレフィン類の連続気相重合方法に関する。

とくに、本発明は、攪拌器を具備した気相重合槽中で、攪拌条件下に流動床層を形成させながら連続的に気相重合を行うオレフィン類の気相重合方法に於て、

(i) 該攪拌器の攪拌翼の高さ上端部が該流動床層区域中に埋没する状態で該区域を攪拌しな

がら気相重合を行うこと、

- (II) 該流動床層区域中で且つ該攪拌翼高さ上端部を超える位置に設けた流動床層区域内圧力検出端と、該流動床層区域より上方の上部空間区域に設けた上部空間区域内圧力検出端とにより、該両区域間の差圧を検知し、この検知された差圧に応じて、該流動床層区域高さがほぼ一定に維持されるように、該区域からオレフィン重合体を抜き出すこと、を特徴とするオレフィン類の連続気相重合方法に関する。

攪拌器を具備した気相重合槽中で、触媒を含有するオレフィン重合体粒子層の中に、ガス状オレフィンを吹き込むことによつて流動床層を形成しつつ連続的にオレフィン類を気相重合させることは公知である。

この際、微細なオレフィン重合体粒子や触媒粒子のエントレインメントを防止するため、ガス流速を小さくし、その代りに機械的攪拌によつて流動層を攪拌して良好な混合状態を得ようとする試みも知られている。しかしながらこのような試み

検出端を設けた場合には、流動床層区域上端が圧力検出端に達したときに、上記上部空間区域との差圧が生ずることにより、これを検知し、この検知された差圧に応じて重合体排出弁を開いて重合体を抜き出し、そしてこの抜き出しに応じて流動床層区域の高さが低下して上記他方の圧力検出端より低レベルになると、上記上部空間区域との圧力差がなくなることにより、これを検知して該重合体排出弁を閉じるというコントロールシステムを採用せざるを得ないが、このような手段による場合には、流動床層区域高さの微調整を可能とするようなコントロールが操作上不可能であつて、流動床層区域高さの変動がかなり大きくなり、安定した運転がし難いという欠点があることがわかつた。

一方、流動床層区域内に上記他方の圧力検出端を設けた場合には、その設置の位置によつて検出端が攪拌機の影響を受けるために正確に圧力が検知されず、したがつて流動床層区域高さを一定に調節することが困難となることがわかつた。更に

にもかかわらず、流動床層内の混合状態を均一にすることが困難であるため、オレフィン重合体の塊状物が生成して、ガス吹込口やオレフィン重合体抜き出し口を閉塞させ、長期間の運転を不可能ならしめることが多い。また、このような気相重合を連続して行う場合、流動床層区域の高さをできるだけ一定に維持するようにオレフィン重合体を抜き出すことが均質な重合体を得、かつ安定な運転を行うために必要である。

そのためには、流動床層区域高さを計測し、それを一定に保つように重合体排出弁の開閉を調節することが考えられる。本発明者等は、このような着想にもとずいて、流動床層区域高さを計測する方法として気相重合槽内に上下2個所の圧力検出端を設け、その一方は流動床層区域より上方の上部空間区域中に、他方は流動床層区域上端又は流動床層区域内に設け、両者の差圧を測定することによつて、流動床層区域高さを求める方法を試みた。

その結果、流動床層区域上端に上記他方の圧力

該検出端に詰りが生じ易く、測定が不能となる場合さえでてくる不都合のあることがわかつた。流動床層区域の攪拌状態が不充分なところで計量すればこのような恐れはないが、そのような状態を生ずるような攪拌条件を採用したときには、均一な流動床状態の形成が阻害されるため、安定な重合が行われず、塊状重合体の生成するトラブルがあることがわかつた。

ところが、更に検討を続けた結果、前記(I)及び(II)を充足する条件下に、上記差圧の検知を行う方法を採用することにより、流動床層区域の高さをほぼ一定にコントロールすることができ、しかも流動床層区域の良好な混合状態が得られ、安定した重合が可能となり、塊状重合体の生成や重合体の壁付着のトラブルが防止できることが発見された。従つて、本発明の目的は、オレフィン類の改善された連続気相重合方法を提供するにある。

本発明のオレフィン重合は、定常状態においては、オレフィン重合体および触媒からなる流動床層区域へ、攪拌条件下に、触媒を連続的に供給する

とともに、ガス状オレフィンを該流動床層区域の下部から吹き込むことによつて流動状態を維持し、かつ重合を行わしめる。流動床層区域内は、攪拌機、好ましくはイカリ型(アンカー型)攪拌機によつて攪拌し、これにより横方向においても良好な混合状態を得ることができる。

流動床層区域の下端部(底部)は好ましくは多孔板となつており、ガス状オレフィンの均一な分散を助けるとともに、重合体粒子等の落下を防止する。分子量調節の目的で水素を用いることができるが、ガス状オレフィンと共に流動床層区域下端部から供給してもよく、あるいは流動床層区域内に直接供給してもよい。

重合器の流動床層区域は、裁頭円錐状又は円柱状のものが好ましく使用される。本発明において用いられる攪拌器、好ましくはイカリ型攪拌機は、これら裁頭円錐状、円柱状等をなす流動層の底面(通常は多孔板からなる)および側壁面に近接して攪拌翼が回転する構造となつており、回転軸から流動床層区域の底面に沿つて側壁部近

もし攪拌翼の上部の一部が流動床層区域から露出して上部空間区域に延びていると、その部分でオレフィン重合体の付着や塊状化が起こり、安定運転を妨げる。また、流動床層区域高さを前記好ましい範囲よりも高く維持すると、流動床層区域全系の混合が不十分となり、壁付着等を起こすおそれがあるため、上記好ましい範囲で適宜に選択するのがよい。イカリ型攪拌器を用い、流動床層区域高さを好ましくは前記範囲内の適当な位置に調節することによつて、重合体の壁付着や塊状化を防止することが可能でしかも安定した運転を行うことができる。

さらに、このような構成をとることにより差圧方式による流動床層区域高さを正確に測定することもできるようになり、したがつて、該区域高さをほぼ一定に保つように、検知された差圧に応じてオレフィン重合体抜き出し弁の開閉を行うように指示することによつて、自動制御が可能である。すなわち流動床層区域内と上部空間区域の差圧を測定すれば流動層高さを測定することが可能であ

刃まで伸び、そこからさらに側壁部に沿つて立上つて伸びる攪拌翼を複数枚有する構造をなしているのが普通である。複数枚有する攪拌翼の高さは必ずしも同一である必要はない。イカリ型攪拌機はまた上記のような基本構造を有している限り、補助的な攪拌翼が設けられていたり、その他の変更態様設計のものであつてもよい。

オレフィン類の重合時において、流動床層区域高さが、攪拌器の攪拌翼の高さ上端部までの高さの好ましくは1.02ないし1.4倍、より好ましくは1.02ないし1.2倍となるように維持し、しかも好ましくはできるだけ流動床層区域高さの変動がなく、ほぼ一定に維持できるようにオレフィン重合体を連続的又は間欠的に抜き出すのがよい。攪拌器の攪拌翼の高さ上端部までの高さとは、流動床層区域底面から該攪拌翼の上端部までの距離であつて、複数の攪拌翼を有し且つその高さが異なる場合には、もつとも高いものを基準とする。

本発明においては、このように攪拌器の攪拌翼を流動床層区域内に埋没させるように運転する。

る。しかし一般に流動床層区域内の圧力検出端は詰り易く、しかも攪拌機の影響を受け易い。ところが上記のように流動床層区域高さを攪拌翼の高さ上端部までの高さよりも好ましくは1.02ないし1.4倍程度の高さに維持し、該流動床層区域中で且つ攪拌翼高さ上端部を超える位置に流動床層区域内圧力検出端を設置すると、詰りもなく、しかも攪拌機の影響も受けず、したがつて正確な測定が長期間に亘つて行うことが可能となる。この結果、流動床層区域内圧力検出端と上部空間区域内圧力検出端とにより、該両区域間の差圧を検知し、この検知された差圧に応じて流動床層区域高さをほぼ一定にするように、オレフィン重合体を抜き出すことが可能であり、長期間連続運転を自動的に行うことができる。流動層側の圧力検出端の位置は、好ましくは攪拌翼の高さ上端部までの高さの1.05ないし1.15倍の高さにするのがよい。

本発明においては、流動床層区域内圧力検出端の少し上部にさらに他の圧力検出端を設け、これと流動層上部の圧力検出端との差圧を測定し、流

動床層区域高さの上限をこの差圧によつて制御する態様を、前記した制御と組合せて採用してもよい。

本発明におけるオレフィン重合は、オレフィンの単独重合のみならず、オレフィン同志の共重合、オレフィンとジエンの共重合なども包含する。オレフィンの例としては、エチレン、プロピレン、1-ブテン、1-ペンテン、1-ヘキセン、4-メチル-1-ペンテン、1-オクテン、1-デセンなどを例示することができる。とくにエチレン又はプロピレンを主体とし、例えばこれら単量体を90モル%以上で含有する結晶性重合体の製造に好適である。

重合触媒としては、チーグラ型触媒、フィリップス型触媒など種々の触媒系を使用することができる。例えばチタン、バナジウム、クロム、ジルコニウムなどの化合物を触媒成分として用いることができる。とくにマグネシウム化合物に担持されたチタン触媒成分と有機アルミニウム化合物触媒成分を使用すると触媒活性が大きいので好適

してもよい。液状のオレフィンを供給する場合には、流動層より上方に供給するのが好ましい。

オレフィン重合体は流動床層区域の側面から、流動層高さが一定となるよう連続的又は間欠的に抜き出される。このような方法を採用して連続重合を長期間行うことができる。

本発明の一実施態様を第1図に示す。予備重合槽1においてマグネシウム化合物に担持されたチタン触媒成分と有機アルミニウム化合物成分を用いてオレフィンを予備重合した後、管11を介して連続的に気相重合槽の流動床層区域3に供給する。追加の有機アルミニウム化合物を管12から気相重合槽の流動床層区域3に供給する。気相重合槽の反応床である流動床層区域3は、イカリ型攪拌機4により攪拌する。ガス状オレフィンは凝縮器6で凝縮しなかつたものを管13を通り、あるいは新たに管14を通つて重合槽の下部に供給し、多孔板5を通つて流動床層区域3に入り、反応床を流動させるとともに重合に使用する。分子量調節に使用される水素は、管15を通り重合槽に供給す

である。これら触媒系についてはすでに広く知られている。重合においては、分子量、分子量分布、立体規則性などを制御する目的で、水素、電子供与体、ハロゲン化合物、その他各種添加剤を使用することができる。これら触媒成分や添加剤は、重合器の任意の場所に供給することができる。重合においてはまた除熱目的のため、易揮発性の不活性化炭化水素を共存させることもできる。これらは重合器中で気化することによつて除熱目的を果す。

オレフィンの重合温度は、オレフィンの種類によつても異なるが一般には約30℃ないし約90℃程度の温度範囲が採用される。また反応圧力は、オレフィンの液化する圧力より小さければ任意の圧力でよく、例えば約2ないし約30kg/cm²・gである。

オレフィンは流動床層区域下部から、線速度が1ないし60cm/sec、とくには約3ないし約40cm/secとなるように吹込むのが好ましい。重合熱除去のため、液状のオレフィンを重合器に供給

る。重合槽から排出される未反応オレフィンは管16を通り凝縮器6で凝縮させ、ドラム7から管17を通り、散布部18から反応床に散布させる。

流動床層区域3の高さは、上部空間区域2に検出端を有する低圧側ライン20と流動床層区域3中で且つ攪拌翼高さ(h₁)上端部を超える位置に検出端を有する高圧側ライン21の差圧をレベル計23で測定し、流動床層区域高さ(h₂)を一定に保つように、レベルコントロールバルブ24の開閉を指示して重合体を管19から抜き出す。高圧側ライン21の詰りを防止するため管22よりバージガスを流しておくのがよい。

実施例 1

<チタン触媒成分の調製>

市販の無水塩化マグネシウム30g、安息香酸エチル7.5mlおよびメチルポリシロキサン(粘度20c. s. (25℃)) 4.5mlを窒素雰囲気中、振動ボールミルで40時間接触させた。得られた固体処理物20gを200mlのT1C₄中に懸濁させ、

80°Cで2時間攪拌下に接触した。反応終了後、デカンテーションにより上澄部を精製ヘキサンで洗浄した。上澄ヘキサン中に塩素が検出されなくなるまでこの操作を繰り返した。得られたチタン触媒成分には原子換算でチタン1.9wt%、塩素65wt%含有されていた。上記操作を数回繰り返すことにより、以下の重合に供した。

<予備重合処理>

前記チタン触媒成分をヘキサン中、1.5mmol/l、トリエチルアルミニウム（以下TEAと略す）6mmol/l、p-トルイル酸メチル（以下MPTと略す）2mmol/l及び添加プロピレンはチタン触媒成分に対して2倍重量で行った。

<ポリプロピレンの気相重合>

前記のように予備重合処理された触媒を使用して第1図に示したフローダイアグラムに従って重合を行った。

気相重合槽の内径は300mm、イカリ型攪拌機4の攪拌翼高さ上端部までの高さ(h_1)は多孔板5から450mm、高圧側ライン21は内径2mmの

SUS製であつて、その流動床層区域内圧力検出端は、重合槽内壁から150mm、攪拌翼上端から30mm上部に挿入した。

イカリ型攪拌機を200rpmで回転させる一方、前記予備重合処理されたチタン触媒成分1mmol/hr（チタン原子換算）、TEA 50mmol/hr、MPT 12mmol/hr、プロピレンガス（循環ガスを含む）を重合槽中4cm/secとなる速度で、またプロピレン液を45kg/hrの速度で散布部18から散布し、重合温度70°C、重合圧力18kg/cm²の条件でプロピレンの連続重合を行った。また流動床層区域高さ(h_2)が多孔板から490mmの高さとなるようにレベル計の指示にしたがつてポリマーを管19から10kg/hrの速度で抜き出した。なお高圧側ラインの詰り防止のため、管22よりプロピレンガスを100Nℓ/hrの速度で供給した。

MI=9.1、n-ヘプタン不溶分が93.3重量%のポリプロピレンを長期間安定して製造することができた。

比較例

高圧側ライン21の検出端の位置を、攪拌翼の高さ及び攪拌器上端部から440mm下部にした場合はいずれもレベルの検出が難しくレベルの増減を検知することができなかつた。

4. 図面の簡単な説明

添付第1図は、本発明方法実施の一態様を示す略示的装置図である。

出願人 三井石油化学工業株式会社
代理人 小田島 平吉（外1名）

第 1 図

